ELECTROLYTIC DISSOCIATION IN NITRIC ACID AS STUDIED BY RAMAN EFFECT*

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ABSTRACT. Electrolytic dissociation in nitric acid was studied by employing Raman Effect first by I. R. Rao. He studied the degrees of dissociation of the acid in different concentrations, relative to the highest concentration. In the present work, the absolute degree of dissociation of the acid is calculated by comparing the intensities of the Raman lines in the spectra of solutions of sodium nitrate and nitric acid of equal molal concentrations, assuming that sodium nitrate dissociates completely even in very concentrated solutions. The results indicate that in the lower concentrations, the increase of dissociation with dilution is very small, whereas in the concentrated solutions, it is rapid. This is explained as being due to the increase in the H-ions in the lower concentrations, which therefore favour the backward reaction.

$$HNO_3 \rightleftharpoons H^+ + NO_3'.$$

INTRODUCTION

It is first suggested by I. R. Rao[1,2] that Raman Effect can be employed to study the electrolytic dissociation in concentrated solutions of strong electrolytes and nitric acid was the first to be studied by him. On studying the Raman spectra of the acid in different concentrations, he observed two sets of lines one decreasing in intensity on diluting the acid and the other increasing in intensity up to a certain dilution. The latter set of lines are found in solutions of nitrates also. He concluded that the first set of lines, the strongest of which is of Raman frequency about 1300, are excited by the undissociated nitric acid molecules, and the latter, the strongest of which is of frequency 1050, are excited by the nitrate ion. On determining the intensities of the lines for solutions of different concentrations he determined the relative degree of dissociation of the acid in different concentrations.

In a previous communication,[3] the author, while reporting similar investigation in solutions of sulphuric acid, suggested that since the sulphates of alkaline elements can be assumed to be completely dissociated in solutions, a comparative study of the intensity of the Raman lines due to the sulphate ion in solutions of the sulphate, acid sulphate and sulphuric acid affords a method

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of obtaining the value of absolute degree of dissociation of the acid in different concentrations. The present work is undertaken to make a similar study in nitric acid, as thus far no one has attempted to determine the absolute degree of dissociation of this substance by a study of its Raman effect.

EXPERIMENTAL

The experimental technique is the same as that employed in the case of sulphuric acid. The Raman spectra of sodium nitrate and nitric acid at different concentrations are taken to compare the intensity of the 1050 line excited by the NO_3' ion in the acid and the salt. Solutions of concentrations from 14.85N to 2.3N are worked with and are exposed for equal times. The intensities of the lines are measured in the usual manner by employing a Zeiss step-filter.

RESULTS

The intensities of the lines are tabulated in the table I.

TABLE I

Concentration (molal)	Intensity if equal exposures are given	No. of NO_3 ions	Percentage degree of dissociation
14.85	29.1	1.96	13.2
13.5	37.8	2.55	18.9
12.15	43 0	2 90	23.9
10.80	53.8	3 63	33.6
7.2	62.1	4.19	58 2
5.7	64.1	4.33	76.0
4.5	57.8	3.90	86.7
3.5	46.1	3.12	89.2
2.3	31.5	2.13	92.6

Since, in the solutions of sodium nitrate, the molecules are assumed to be completely dissociated, the number of NO_3' ions in that solution equals the total number of molecules. Therefore, on dividing the intensity of the 1050 line in the sodium nitrate solution by the total number of molecules of $NaNO_3$, the intensity of the Raman radiation due to each NO_3' ion "a" can be obtained. The intensities of the 1050 line in all the solutions are tabulated in column 2. Dividing these values of the intensities by "a" the number of NO_3' ions "n"

in each of the solutions of the acid is obtained. Dividing this number by the total number of molecules of the acid the degree of dissociation α in each of the solutions is calculated and tabulated in column 4.

To have an idea of the nature of the variation of the electrolytic dissociation of nitric acid with dilution, the degree of dissociation is plotted against the concentration for the different solutions of the acid in figure 1. It is evident from

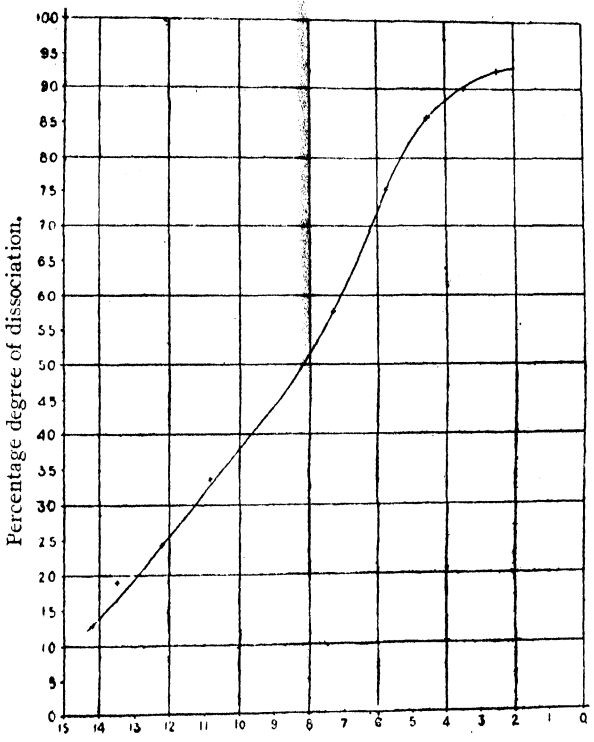

FIGURE 1

the graph that, in the higher concentrations, the rate of dissociation is very large while in the lower concentrations it is less as is conspicuous from the smaller inclination of the curve to the dilution axis for these concentrations. A similar result was obtained in the case of solutions of sulphuric acid and it is explained as being due to the increased number of H-ions formed on dissociation, which favour the backward reaction in the equation in the case of smaller concentrations.

$$H_2SO_4 \rightleftharpoons HSO_4' + H^+.$$

It is quite likely that a similar explanation holds good in the case of nitric acid also. Due to the increase in the H-ions with dilution, the backward reaction in the equation

$$HNO_3 \rightleftharpoons NO_3' + H^+$$

is more favoured than the forward reaction.

In this connection, one point requires elucidation. It is assumed that sodium nitrate dissociates completely in solution, and the above calculation of the absolute degree of dissociation of the acid does not contemplate any polymerisation of the NO_3' ions. To test this point, solutions of sodium nitrate of concentrations 4.5N, 3.5N and 2.3N are taken and exposed for times proportional to dilution. The intensities of the 1050 line in solutions are measured and are found to be in the ratio 224.5 : 227.5 : 228.1. From the above values of the intensity, it is seen that they are nearly equal within the range of experimental error, and they confirm the assumption that sodium nitrate is completely dissociated at all concentrations and that there is no polymerisation of these ions.

But, Sidgwick [4,5], while studying the depression of freezing point of the solutions, finds that, on calculating the depressions on the assumption that the salts are completely dissociated, the values are too low. For example, with the solutions of alkaline nitrates all of the same concentration 3N, he found that, while the calculated value of the depression of the freezing point comes out to be as high as 12°.4C, the experimental values are between 6°.3C and 9°.0C except for lithium nitrate where it agrees with the calculated value. Agreeing that the laws of dilute solutions cannot be applied to concentrated solutions, Sidgwick opines that the abnormally low value must be due to some polymerisation of the NO_3' ions into N_2O_6, in the concentrated solutions. The values of the depression of the freezing point calculated on this assumption will be too low and he thinks that this may be due to the hydration of the anions, and the high value of the depression in the lithium nitrate solution may be due to the high capacity of the Li^+ ion to form a hydrate in virtue of its smallness and positive charge and the fact that it is the only alkaline nitrate that forms a hydrate in the solid form, adds strength to this view.

If, as is assumed by Sidgwick, it is true that NO_3' ions polymerise in solution, the method adopted in this work for the calculation of the absolute degree of dissociation of nitric acid is based on a wrong foundation. Supposing that there is a certain number of polymerised NO_3' ions in 4.5N solution, of sodium nitrate, and that when the concentration is reduced, a depolymerisation of some of the N_2O_6 molecules is to be expected as the polymerised molecules always do so on dilution. Also, 2 sets of Raman lines, one corresponding to N_2O_6 type of molecules and the other due to NO_3 type are to be expected as in the case of solutions of acetic acid where Koteswaram[6] found that there is one set of lines corresponding to polymerised molecules and another set corresponding to the single molecules, the former set of lines being more prominent in concentrated solutions and as the solution is diluted, they become feeble, while the latter set becomes strong.

We do not find a similar behaviour in the case of Raman lines of nitrate solutions, and therefore we may assume that no polymerised molecules exist.

But, by some chance, the radiations excited by both the types of molecules may happen to be identical, in which case, the intensity of the 1050 line increases in intensity as the dilution is increased due to increase in the number of NO_3 ions formed on depolymerisation. As is already pointed out, the intensity of 1050 line did not change with dilution, thereby indicating that there is no increase in the number of NO_3 ions. Therefore, it can be safely concluded that the NO_3 ions are not polymerised, and the calculation of the degree of dissociation of nitric acid given in table I, based on this assumption, is correct.

The smaller values for the lowering of the freezing points may be due to the lowering of the osmotic pressures of the solutions due to the inter-ionic forces, as explained by Debye and Huckel.

In conclusion, the author wishes to record his grateful thanks to Dr. I. Ramakrishna Rao under whose direction the present work is undertaken.

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